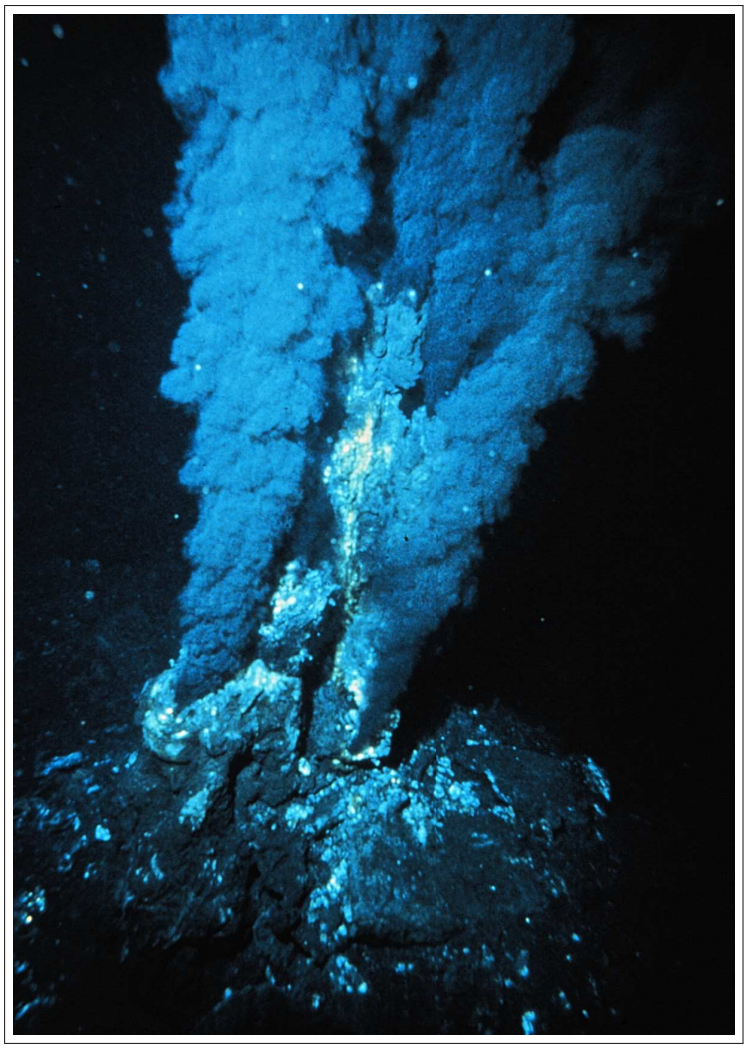
Chapter 2

Supercritical Fluids



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Abstract

Supercritical fluids receive more and more attention in science and industry due to the versatile possibilities for application. This versatility results from the adjustable properties of supercritical fluids. The applications for supercritical fluids range from extraction, particle formation, reactions, cleaning to dyeing.

The physical phase, in which one compound exists at a given temperature and pressure, determines the properties, the behavior and the structure of that compound. Therefore, an understanding of the phase and its effects on matter is essential to work within this phase and to apply it for research and industry.

In this chapter, the characteristics of a supercritical fluid and its properties are introduced. Applications with supercritical fluids such as carbon dioxide are mentioned. In order to explain the usage of supercritical water as medium for the removal of inorganic compounds and desalination, the properties of supercritical water are investigated more thoroughly. In particular, the changes in solvation behavior for inorganic and organic compounds and the difficulties for industrial applications and research due to the harsh conditions of supercritical water are discussed. In conclusion of that, the basic principle of supercritical removal of inorganic compounds is introduced as well as its beneficial aspects. Process options and technical considerations are furthermore introduced and evaluated.

2.1 Introduction

Water is the most abundant compound on Earth, present in all three common phases liquid, solid and vapor. Due to its dipole moment resulting from the difference in electronegativity between oxygen and hydrogen and its ability to form hydrogen bondings with other water molecules (tetrahedral structure) and soluted compounds, water shows unique properties and behavior. This makes water an unusual compound in comparison to other compounds of similar molecular weight and composition (e.g. $\mathrm{H_2S}$ is a gas at ambient state). For water, the boiling and melting point (273.15 resp. 373.15 K), the high heat capacity (4.21 $kJ \cdot kg^{-1} \cdot K^{-1}$), the heat of vaporization (40.65 $kJ \cdot mol^{-1}$) and its miscibility and solvation abilities at ambient state for a vast number of chemical compounds are to be mentioned. These properties are among others the reason for the possibility for the development of life on Earth.

While one is aware of the properties and behavior of water in the three phases liquid, solid and vapor, water also shows interesting and diverting behavior in its supercritical state (Critical temperature T_c = 647 K; critical pressure p_c = 22.1 MPa). This behavior in the supercritical state is the background of this thesis.

2.2 The supercritical state

At the triple point of a chemical compound, three different phases can be distinguished, *solid (s)*, *liquid (l)* and *vapor (v)* (cf. Fig. 2.1). Upon temperature and pressure increase along the vapor-liquid equilibrium curve, both phases coexist. With a further temperature and pressure increase according to the phase boundary curve, the liquid becomes less dense due to the temperature increase. The vapor phase becomes more dense due to the increase in pressure. Resulting from that, the phases become less and less distinguishable when temperature and pressure are increased further. At one point on the boundary curve, only one phase is present in the system. This point is called the *critical point* and the new phase is called the *supercritical fluid phase*. The temperature at the critical point is called *critical temperature* T_c and the pressure *critical pressure* p_c.

The critical properties of a compound depend on its molecular structure. Polar compounds with a strong intermolecular structure due to hydrogen bonding such as water, ammonia and methanol have elevated critical properties in comparison to apolar ones like methane or ethane (cf. Tbl. 2.1). For the usage of supercritical water, these elevated

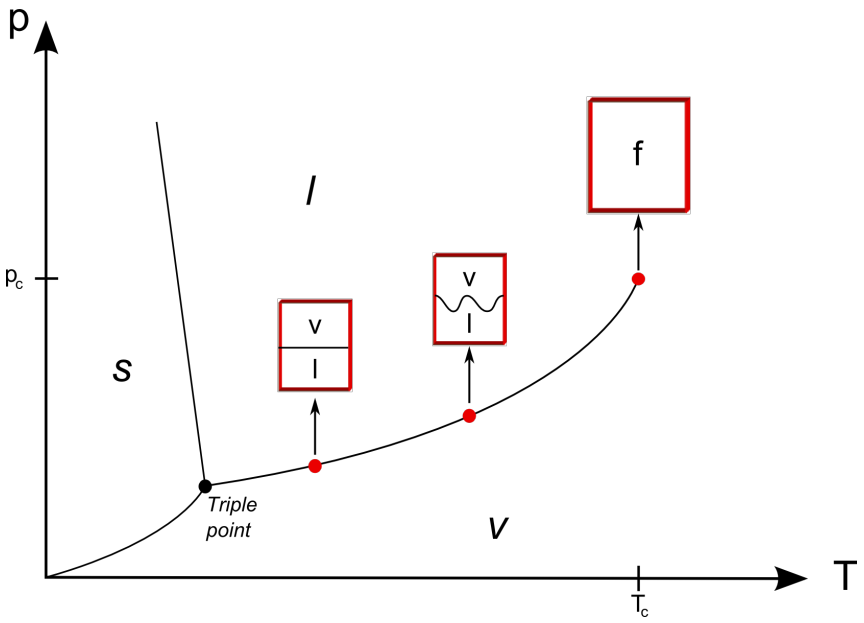

Figure 2.1 ‖ Phase diagram of water

critical properties are to be kept in mind since they result in harsher working conditions and more challenging engineering solutions.

The properties of a supercritical fluid are a mixture of the properties of the liquid and the vapor phase. This includes e.g. density, viscosity, heat conductivity and diffusion rate. Diffusivities are higher than in liquid state, making it for instance interesting for reactions in supercritical carbon dioxide like polymerizations (1). On the other side, heat capacity and thermal conductivity are higher for supercritical water than for steam, turning it thereby into an interesting heat and energy carrier in power plant cycles (2). These properties can be easily adjusted to the needs of a process via temperature and pressure alternation (3; 4).

Next to the tunability, several further aspects make supercritical fluids interesting media for industrial applications. Supercritical carbon dioxide, the most commonly used supercritical fluid, is cheap, non-toxic, non-flammable, environmentally benign, chemically stable and has easily manageable critical properties. It also has solvent potential for organic components, which increases with increasing polar character of the organic compound. Supercritical water has similar advantages, yet the higher critical properties and the special nature of supercritical water have been regarded as a major problem for industrial applications and research so far. Although continuous efforts were made in the last decades, the amount of experience in this area as well as reliable property data and tools for investigation and measurement at these conditions are limited. Therefore,

Table 2.1 ‖ Critical properties of several compounds (3)

	Critical temperature T_c/K	Critical pressure p_c/MPa
Carbon dioxide	304	7.4
Ethane	305	4.9
Propane	370	4.3
Water	647	22.1
Ammonia	406	11.4

projects on supercritical water are still mainly in a pilot plant stage.

Both supercritical carbon dioxide and supercritical water are often referred to as *green solvents*. The other mentioned supercritical fluids are used only for special applications due to safety reasons (3).

Table 2.2 ‖ Properties of water in the liquid, supercritical and vapor phase (5)

	Liquid	Supercritical	Vapor
Density / $kg \cdot m^{-3}$	998	125.1	0.46
Dyn. viscosity / $N \cdot m^{-2} \cdot s$	$1{\cdot}10^{-3}$	$2.9 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$
Thermal conductivity / $W \cdot m^{-1} \cdot K^{-1}$	0.598	0.102	0.033

2.3 Applications of supercritical fluids

The range of applications for supercritical fluids has been growing in the last decades as result of increased understanding and growing industrial experience on these systems. While supercritical carbon dioxide still represents the most frequently used supercritical fluid, supercritical water is considered due to its unique properties as optional medium for example for reactions and particle formation. Therefore, supercritical water gains more and more attention and importance (6).

In the first industrial applications of supercritical fluids, propane and pentane were used. Introduced in 1936, a process for the refinement of lubricating oils used propane as solvent of choice. This process was operated in the vicinity of the critical point of propane, yet still subcritical (7). In 1946, the *Solexol* proccess was introduced for the

purification of vegetable oil (to produce triglycerides) and fish oil (to produce vitamin A). Supercritical propane was used as solvent (8). As refining technology in the petrochemical industry, supercritical pentane was used since 1976 in the *ROSE* process (Residuum Oil Supercritical Extraction) to extract low molecular weight components (9).

The first major industrial application of supercritical CO_2 was the removal of caffeine from coffee beans in the last 1970's / early 1980's (10–12). Later on, multiple comparable extraction and separation processes for the removal of organic compounds like for instance ethanol, fragrances and oils were developed (13; 14). Next to these, particle formation in supercritical carbon dioxide has received a high amount of attention. This method offers the option to produce particles of a defined size and size distribution on a micro-scale and even nano-scale (15–18). Also the usage as a reaction medium for reactions like polymerizations (1; 19; 20) as well as hydrogenation, hydroformylation and alkylation (21). Further applications range from dyeing of textiles (22; 23), drying of aerogels, microelectronics and other sensitive devices (24; 25) to analytical methods like chromatography (3; 26).

One focus for applications based on supercritical water was on oxidation reactions, the so-called *Supercritical Water Oxidation*[1]. SCWO makes use of the increased solubility of supercritical water for oxygen or other oxidants and organic compounds in order to decompose and destroy the organic compounds (27–29). The range of treated compounds includes waste sludge (30; 31), chemical warfare agents and rocket propellants (32) and industrial waste water streams (33). Industrial applications on SCWO have not exceeded the status of pilot plants so far due to operational problems like corrosion and scaling (27; 34). Similar to supercritical carbon dioxide, also supercritical water is considered as medium for particle formation (35; 36). Here, mainly inorganic compounds like oxides are investigated (33; 37; 38). As a result of higher heat capacity in comparison to steam, supercritical water is used as heat carrier in power plants since the 1930's to increase the efficiency in comparison to subcritical steam cycles (2; 6; 39). Also, the usage of supercritical water in the next generation of nuclear power plants is considered to be a feasible option (2; 40). For a large number of chemical reactions, which are currently operated with organic solvents, supercritical water is borne in mind as an alternative (6; 41; 42). Here, the benign and non-toxic nature, the occurrence of water in a multitude of systems as reactant or by-product and the comparably easy separation step of water from organic compounds are the main supportive arguments for supercritical water as medium of choice (41). As a further approach, gasification of

[1] In the following abbreviated with **SCWO**

biomass in supercritical water offers several benefits, which are not given by standard gasification units (43–45). The most prominent one is the avoidance of a drying step of the biomass prior to the actual gasification. This step uses a certain percentage of the gained energy in the gasification step. Also a better control of the quality of the gasification products is possible since this can be regulated by the conditions in the system and a correct choice of the catalyst (44).

The afore mentioned applications all have to struggle with the presence of inorganic compounds, which can lead to scaling, corrosion and equipment failure. Therefore, a sound knowledge of the behavior of inorganic compounds in supercritical water is necessary. As a result, processes like the ones mentioned above could be optimized to overcome the existing problems.

2.4 Solvation behavior of supercritical water

Next to the property changes mentioned, also the internal structure of water changes in the supercritical state. Hydrogen bondings, responsible for the orientation of the molecules towards each other, start to diminish and to weaken when water enters the supercritical state (41; 46; 47). Thereby, several characteristics of water change like the excellent solvation of inorganic compounds and salts.

An indicator for these changes is the dielectric constant. The dielectric constant is a relative measure for the polarity of a fluid and resulting from that an indicator for its solvation behavior. Water at ambient state has a dielectric constant of around 80, which decreases to appr. 2 at 25 MPa and 700 K (cf. Fig. 2.2). As a consequence of this, water loses its polar character and turns into a non-polar fluid. Thereby, the solvation ability for inorganic compounds is diminished and salts can not be solved easily in supercritical water. On the other hand, due to its non-polar character supercritical water is a fair solvent for organic compounds. This change of solvation behavior is applied in several applications like reactions and SCWO (27; 41). Another aspect arising from the absence of hydrogen bondings is the presence of ions in supercritical water. Since a decrease in strength of hydrogen bonding occurs, ions tend to lose their hydration shell and merge to a large percentage to neutral molecules and complexes (48–50).

Due to changes in hydrogen bonding and solvation behavior, solubilites of salts drop by several orders of magnitude upon entering the supercritical state (cf. Fig. 2.3). If a feed stream with a certain concentration of salt is brought to a state above the critical point, the exceeding amount of salt starts to form a solid phase. Depending on the

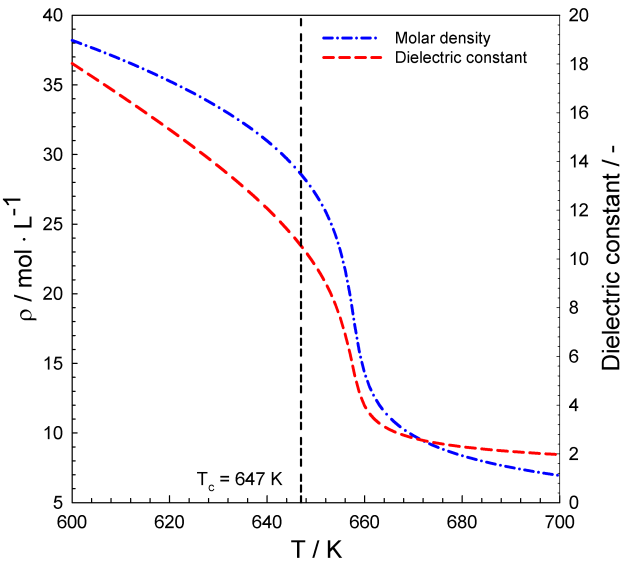

Figure 2.2 ‖ The dielectrical constant of water at 25 MPa (51)

degree of supersaturation, precipitation or crystallization occurs. The concentration of the salt in the fluid phase decreases till equilibrium between solid and fluid is established.

The formation of a solid phase can lead to severe problems in industrial applications (28; 29). The formed crystals can accumulate on the walls and pipings and lead to erosion and scaling. Thereby, increased pressure drops and equipment failure are possible. Furthermore, the risk of corrosion is increased as a a result of the formation of local elements on the surrounding surfaces (52). On the other hand, a formation of a solid phase provides an option to remove this solid phase from the bulk stream.

2.5 Removal of inorganic compounds in supercritical water

The decreased solubility of inorganic compounds in supercritical water leads to a formation of a solid phase within the supercritical fluid phase. These compounds can be separated and removed from the fluid phase via common solid separation technology like gravity separators, membranes and hydrocyclones (34; 53; 54). Both phases, the fluid water phase as well as the solid salt phase, can be seen as value products of such a process. By removal of these inorganic compounds, the water phase can be used afterwards as drinking and usage water. If salts are the target product of such a process, a removal

of these compounds from the fluid phase without the need of a common evaporative technique is possible. Furthermore, it is an feasible option to separate the different salt fractions from each other since the solubility of each salt is depending on the current state in the system. Thereby, this separation can be controlled by adjusting the temperature and the pressure to the necessary conditions. This technique is also interesting for other technologies based on supercritical water (e.g. SCWO, gasification of biomass), where inorganic compounds lead to severe problems like catalyst poisoning, scaling and corrosion (28; 55).

The driving force for formation of a solid phase is the difference between the equilibrium concentration of a salt at a temperature T and pressure p and the actual concentration of the salt (cf. Fig. 2.3). The larger the difference between both concentrations, the higher the supersaturation of the system. A high degree of supersaturation leads to rapid precipitation and to further nucleation and crystal growth. This solid material can be removed from the fluid stream via common solid separation principles. Yet, high supersaturation can lead to the formation of very small crystals. Thereby, a separation of these crystals can represent a challenge for the design of the separation step. This has to be kept in mind for the industrial application of this principle and the evaluation of possible feed streams.

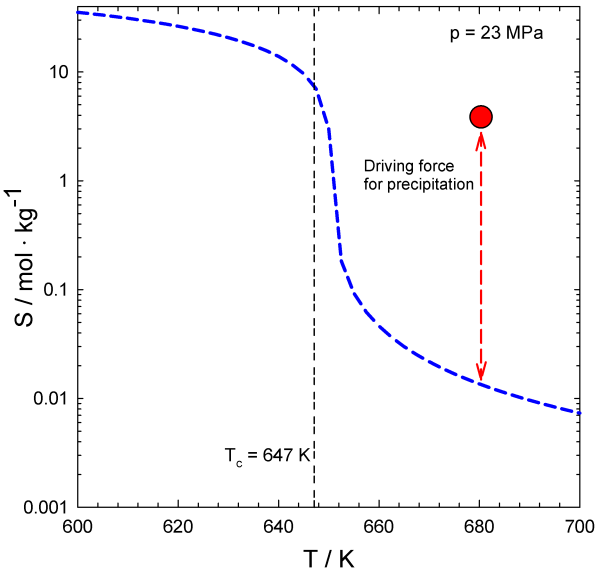

Figure 2.3 ‖ The solubility of NaCl at 23 MPa as a function of temperature (50), dashed line represents the solubility of NaCl

2.6 Process options

Although water is seen as the essential product of a desalination process, the contained salts of saline streams can nevertheless represent a desirable product. In the following, basic concepts for the application of the separation principle are introduced to produce fresh water as the main product as well as for different salt fractions as main product. The latter is an interesting approach to treat aqueous streams with high load of valuable salts to obtain these salt fractions while water is considered as a by-product (e.g. $\mathrm{MgCl_2}$, heavy metals).

2.6.1 Water as value product

In Figure 2.4, a conceptual scheme in unit operations for a separation process based on the property changes described above is presented[2]. The feed stream is brought to a supercritical state in an energy input unit. The following unit operations consist of a crystallization / precipitation step and a solid / fluid separation step. The final step is an energy recovery unit. Furthermore, it is possible to recycle parts of the product streams in order to inoculate the crystallization step and thereby to enhance the efficiency of this step. The products of this concept are a) a liquid phase with a salt concentration according to the solubility in the supercritical steps before and b) a solid phase consisting of salts.

One of the major advantages of this concept is that no additional waste stream is produced like in membrane and evaporation techniques (retentate / bottoms). Contrary, two separate phases - one solid, one liquid - are produced. The yield in relation to the feed water intake can be significantly increased. The quality of the liquid phase is depending on the system parameters temperature and pressure and the specifications and efficiency of the separation and crystallization step. A further aspect is the high degree of possible energy recovery. Although a certain amount of energy is necessary to run the process, a large part of this energy can be recovered. Methods for energy recovery from pressurized streams are used for all major membrane installations with a high efficiency (56; 57). Additionally, supercritical water has been used and is still used as a heat carrier in steam cycles of power plants. Here, the higher heat capacity in comparison to steam makes SCW the preferred medium (2; 39).

Contrary to membrane and evaporation technologies, no energy is lost due to the

[2]In the following called *Supercritical Removal (of inorganic compounds)*; **SCR**

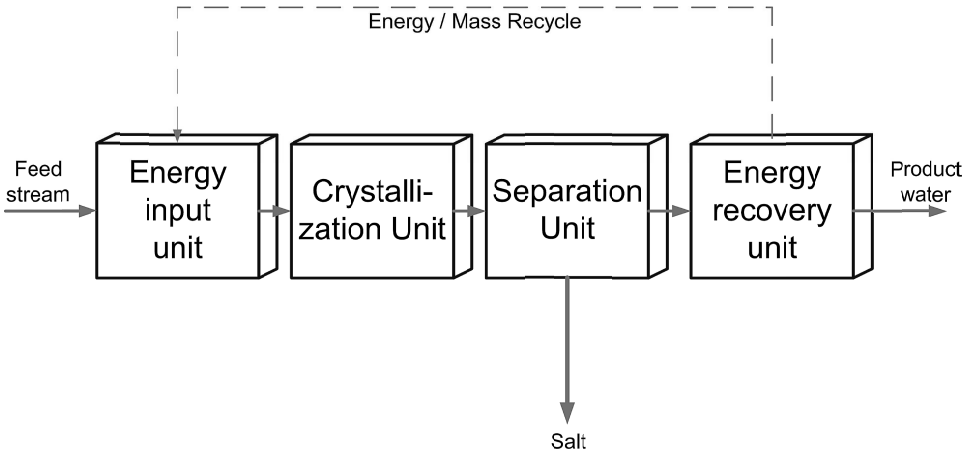

Figure 2.4 ‖ Conceptual scheme of a SCR process in unit operations

separation mechanism. For RO, the pressure drop across the membrane while for evaporation the heat of evaporation cannot be recovered. The energy necessary to bring the feed stream in a supercritical state can be recovered to a high percentage by usual means (heat exchanger and pressure recovery units; 80 - 95 % recovery). Organic material (e.g. bacteria) is decomposed at these conditions. Therefore, the dosing of additional chemicals to avoid fouling and biological growth can be kept to a minimum by the conditions of the process itself.

Next to standalone applications, also combinations with membrane or evaporation concepts are possible (cf. Fig. 2.5). The benefit of these combinations is next to the usage of the combined infrastructure (e.g. pre-treatment, energy recovery) also the avoidance of a brine stream, which is unavoidable for pure membrane / evaporation concepts. The disposal of such a brine stream is next to the energy demands one of the crucial issues of nowadays desalination processes. Especially at locations, where the usual treatment of these streams is not feasible - disposal in the open sea - like at landlocked locations or at environmentally endangered areas, solutions are necessary for this problem. For the combination of these processes, the SCR step can be applied as pre-treatment and as post-treatment for an evaporation or a membrane unit.

A more detailed discussion of possible process options can be found in Chapter 7.

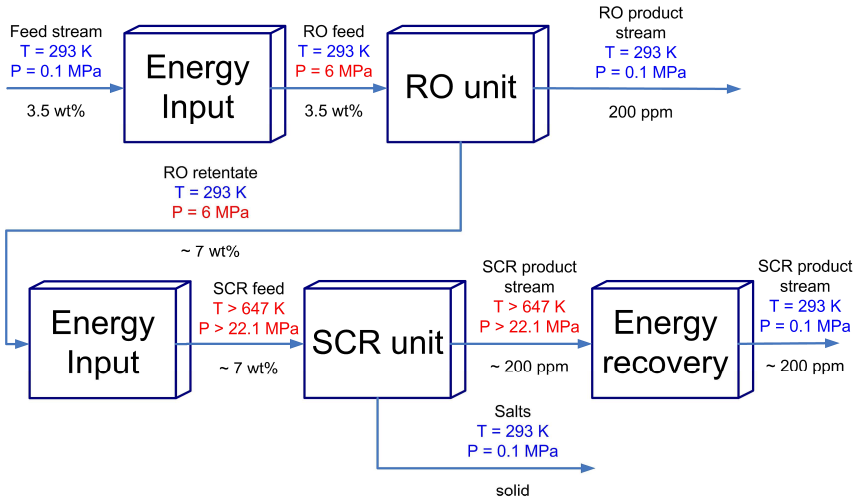

Figure 2.5 ‖ The usage of SCR as post-treatment for a RO unit

2.6.2 Process conditions

The energy demand to bring a stream to a supercritical state is another important aspect that needs attention. If this demand can be kept at a minimum while still achieving the quality demands for the product streams, less energy needs to be recovered. This minimizes the loss of energy due to efficiencies of the heat and pressure recovery units. In order to evaluate preliminary possible process conditions, the pressure-enthalpy diagram of water can be used (cf. Fig. 2.6). In this diagram, the isotherms are represented as dashed lines. The region within the black curve is the steam region consisting of liquid and vapor with increasing vapor content with increasing enthalpy. The critical point can be found on top of the steam region. The supercritical region can be found at pressures higher than the critical pressure (a parallel to the x-axis through the critical point) and temperatures above the critical temperature (any isotherm above the critical isotherm).

As can be seen from Figure 2.6, tremendous differences in the enthalpies exist for conditions in the supercritical regime ($T \geq 647\ K;\ p \geq 22.1\ MPa$). States with low yet supercritical pressures have a higher enthalpy than states with a higher pressure at isothermal conditions. Therefore, it might be interesting in regard to the energy demand of the total process to investigate higher pressure states as the condition of choice. Higher temperature states with a constant pressure result in a higher enthalpy at that state.

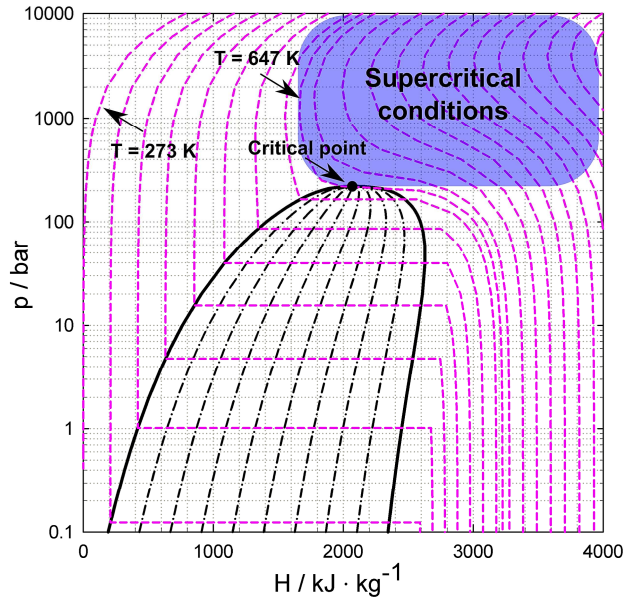

Figure 2.6 ‖ Pressure - Enthalpy diagram of water (5)

In order to optimize the conditions for such a process, several factors have to be carefully evaluated. Next to the solubilities of different salts, which result from the quality demands of such a process, and the minimum in energy consumption, which is a must for an economically and ecologically sustainable process, further engineering considerations are important. Due to increased temperature and pressure and the aggressive nature of supercritical water (34; 52), the material of choice has, depending on the conditions of the process, to withstand harsh conditions and mechanical stress and resistant to corrosion. Corrosion is one of the major obstacles in the industrial applications of supercritical water and has lead to severe problems in pilot plants for SCWO and gasification. Nevertheless, with the growing experience and on-going research in this field, this issue is assumed to be manageable in future installations (58). In order to avoid corrosion or at least to minimize it, it is possible to adjust the conditions in such a way that corrosion is not supported by high densities and temperatures. Therefore, a careful choice of the process conditions is necessary. As can be seen from Figure 2.7, processes running under subcritical conditions have a higher tendency for corrosion. Processes, which are running under supercritical conditions, yet comparably low temperatures, show less tendency for corrosion (52). Furthermore, the design of the different unit operations depends on temperature and pressure. This makes it a difficult task to actually manufacture these units and may lead to a re-evaluation of the process conditions. Here, the heat transfer units have to be mentioned explicitly since they will encounter precipitation and thereby

the possibility of scaling on the surfaces. Efficient solutions for this issue have to be found.

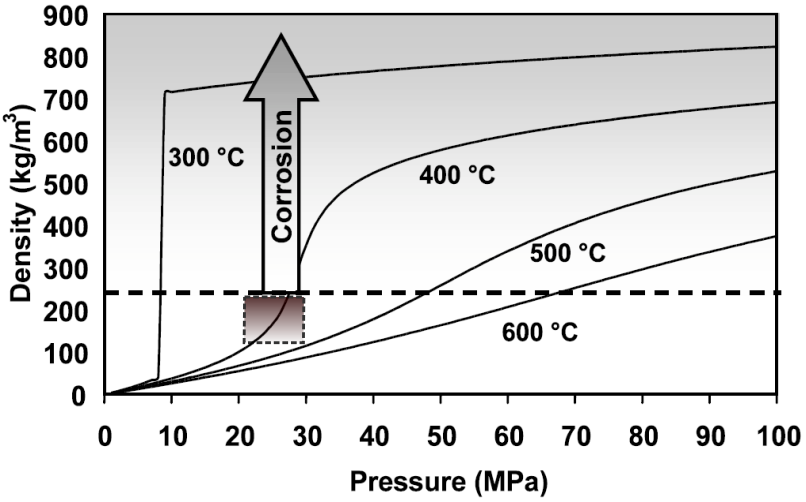

Figure 2.7 ‖ Corrosion tendency as function of the system parameters; boxed area represents expected system conditions (5; 52)

2.7 Conclusions

In this chapter, the supercritical state of a compound was introduced. It was shown that the properties of a supercritical fluid can be beneficial and interesting options for chemical and engineering processes since the properties of a supercritical fluid are adjustable by changes in pressure and temperature.

Supercritical water offers - due to the changes in solvation behavior and solubility for inorganic compounds - an option for a separation of inorganic compounds in a solid form from the remaining bulk fluid stream. Here, the difference between the actual solubility of a compound in a supercritical state and the concentration in the bulk stream is the driving force for such a separation. The excess amount crystallizes and forms an additional solid phase. This solid phase can be separated from the fluid. As shown, higher concentrations in the bulk stream are supporting the separation by increasing the driving force.

A major benefit of this separation principle is the avoidance of an additional liquid waste stream. Therefore, several process options were introduced utilizing this separation

principle to overcome this drawback. Here, it has to be stated that a stand-alone is possible as well as a hybrid solution by combining this principle with existing technologies like RO or MSF. Furthermore, a fractionation of the present salt fractions is possible as a result of the difference in solubilities in supercritical water.

For a further evaluation of the process, several application-specific aspects have to be discussed and evaluated before a further scale-up is possible. Furthermore, the process conditions and corrosion have to be mentioned next to engineering questions to withstand the harsh conditions present in this process.

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